Microwave Spectra and Molecular Structures of Methyl Cyanide and Methyl Isocyanide*

Myer Kessler,† Harold Ring,‡ Ralph Trambarulo, and Walter Gordy

Department of Physics, Duke University, Durham, North Carolina

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Certain of the pure rotational lines of methyl cyanide and methyl isocyanide have been measured and the following molecular properties have been obtained. The moments of inertia, I_B, $\times 10^{-4}$ g cm^2, are: for $C^{12}H_3C^{12}N^{14}$, 91.20_{34}; for $C^{12}H_3C^{13}N^{14}$, 91.24_{86}; for $C^{12}D_3C^{12}N^{14}$, 106.76_{66}; for $C^{12}D_3C^{13}N^{14}$, 106.89_{48}; for $C^{12}H_3N^{14}C^{12}$, 83.45_{50}; for $C^{12}H_3N^{14}C^{13}$, 86.52_{77}; for $C^{12}D_3N^{14}C^{12}$, 97.75_{79}; and for $C^{12}D_3N^{14}C^{13}$, 101.33_{91}. The molecular dimensions are: for CH$_3$CN, $d_{CH} = 1.092$A, $d_{CC} = 1.460$A, $d_{CN} = 1.158$A, and $\angle HCH = 109°8'$; for CH$_3$NC, $d_{CH} = 1.094$A, $d_{CN} = 1.427$A, $d_{NC} = 1.167$A, and $\angle HCH = 109°46'$. The nuclear coupling for N^{14} is -4.35 Mc/sec. in CH$_3$CN and is $< |0.5|$ in CH$_3$NC.

I. INTRODUCTION

METHYL cyanide and methyl isocyanide have been previously investigated by means of infra-red[1] and Raman spectra[1] as well as by electron diffraction.[2-4] The infra-red and Raman spectral studies have shown that both methyl cyanide and methyl isocyanide have symmetric-top configurations. Electron diffraction work has provided values, accurate to about two percent, for the distances between the heavier atoms. The present work allows a more accurate evaluation of these distances, and in addition provides the first determination of the CH distances and of the HCH bond angles. An evaluation of the nuclear quadrupole coupling of N^{14} is also made. Preliminary results[5] for the most abundant isotopes were reported earlier.

II. EXPERIMENTAL PROCEDURE

The lines were detected by a method previously described[6] and were measured with a frequency standard[7] monitored by station WWV. Most of the measurements were made at dry ice temperatures and at pressures of about 5×10^{-3} mm of Hg.

The samples of methyl cyanide and of methyl isocyanide were synthesized essentially by the methods of Guillemard.[8,9] Methyl isocyanide was prepared by heating 0.4 g (2.8 mmole) of methyl iodide with 0.8 g

(6.0 mmole) of silver cyanide at 80°C for four hours in a sealed tube. The resulting product was diluted with several milliliters of water and made strongly basic with potassium hydroxide. The methyl isocyanide was removed by distillation and purified in a vacuum system by successive evaporations and condensations. Methyl cyanide was obtained by heating methyl isocyanide in a sealed tube for four hours at 260°C and purified by fractionation in a vacuum system. Silver cyanide with the C^{13} content enriched to 14 percent and deuterated methyl iodide were used in the syntheses of the appropriate isotopic species.

III. RESULTS

Table I lists the frequencies measured for the different molecules. In methyl cyanide the N^{14} nuclear quadrupole coupling splits the rotational lines into a number of frequencies. A comparison of the calculated and observed hyperfine structure for the $J = 1 \rightarrow 2$ transition of $C^{12}H_3C^{12}N^{14}$ is given in Table II. For methyl isocyanide N^{14} quadrupole splitting was too small to be resolved. Nevertheless, the lines of different K are separated by centrifugal distortions.

Rotational lines of molecules in excited bending vibrational states were also measured. For methyl cyanide the lines of the vibrational state consist of a widely spaced triplet. For the isocyanide the central line of this triplet is split into a doublet with components separated by 2.48 Mc/sec. The structure of the lines for the excited vibrational states has been satisfactorily accounted for by Nielsen.[10] Details of the theory, which is applicable to other symmetric rotators in excited bending vibrational states, may be found in Nielsen's recent paper.[10]

Table III lists the B values, the moments of inertia, centrifugal stretching constants and nuclear couplings. Table IV lists the interatomic distances and bond angles. For each molecule there are four structural parameters. Thus, the four different isotopic species are just sufficient for a complete determination of the structures. The accuracy of these determinations is limited by the zero-point energy effects to about one percent. The equations used in calculating the struc-

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[10] H. Nielsen, Phys. Rev. **77**, 130 (1950).

TABLE I. Observed frequencies for methyl cyanide and methyl isocyanide.

Species	Transition			Frequency[a] (Mc/sec.)
$C^{12}H_3N^{14}C^{12}$	$J=1\to2$,	$K=0\to0$		40,211.16
	$J=1\to2$,	$K=1\to1$		40,210.27
	$J=1\to2$,	For excited vib. state $\omega_8(e)$		40,313.37 40,364.07 40,366.55 40,424.49
$C^{12}H_3N^{14}C^{13}$	$J=1\to2$,	$K=0\to0$		38,783.21
	$J=1\to2$,	$K=1\to1$		38,782.21
$C^{12}D_3N^{14}C^{12}$	$J=1\to2$,	$K=0\to0$		34,327.82
	$J=1\to2$,	$K=1\to1$		34,327.23
	$J=2\to3$,	$K=0\to0$		51,490.90
	$J=2\to3$,	$K=1\to1$		51,490.05
	$J=2\to3$,	$K=2\to2$		51,487.51
$C^{12}D_3N^{14}C^{13}$	$J=2\to3$,	$K=0\to0$		49,671.19
	$J=2\to3$,	$K=1\to1$		49,670.43
	$J=2\to3$,	$K=2\to2$		49,668.07
$C^{12}H_3C^{12}N^{14}$	$J=1\to2$,	$K=1\to1$,	$F=1\to2$	36,793.64
	$J=1\to2$,	$K=0\to0$, $K=1\to1$,	$F=0\to1$ $F=2\to2$	36,794.26
	$J=1\to2$,	$K=1\to1$,	$F=2\to3$	36,794.88
	$J=1\to2$,	$K=0\to0$,	$F=2\to3$ $F=1\to2$	36,795.38
	$J=1\to2$,	$K=1\to1$,	$F=0\to1$	36,796.27
	$J=1\to2$,	$K=0\to0$,	$F=1\to1$	36,797.52
	$J=1\to2$,	For $\omega_8(e)$ excited vib. state with hyperfine structure unresolved		36,942.15 36,903.40 36,870.94

TABLE I. (Continued.)

Species	Transition			Frequency[a] (Mc/sec.)
$C^{12}H_3C^{13}N^{14}$	$J=1\to2$,	$K=0\to0$,	$F=2\to3$ $F=1\to2$	36,777.18
$C^{12}D_3C^{12}N^{14}$	$J=2\to3$,	$K=0\to0$,	$F=3\to4$ $F=2\to3$ $F=1\to2$	47,147.60
	$J=2\to3$,	$K=1\to1$,	$F=3\to4$ $F=1\to2$	47,147.00
	$J=2\to3$,	$K=1\to1$,	$F=2\to3$	47,146.68
	$J=2\to3$,	$K=0\to0$, $K=1\to1$, $K=2\to2$,	$F=3\to3$ $F=3\to3$ $F=1\to2$	47,146.00
	$J=2\to3$,	$K=2\to2$,	$F=3\to4$ $F=3\to3$ $F=3\to2$	45,145.20
	$J=2\to3$,	$K=2\to2$,	$F=2\to3$ $F=2\to2$	47,143.85
$C^{12}D_3C^{13}N^{14}$	$J=2\to3$,	$K=0\to0$,	$F=3\to4$ $F=2\to3$ $F=1\to2$	47,091.05
	$J=2\to3$,	$K=1\to1$,	$F=3\to4$ $F=1\to2$	47,090.41
	$J=2\to3$,	$K=0\to0$, $K=1\to1$, $K=2\to2$,	$F=3\to3$ $F=3\to3$ $F=1\to2$	47,089.43
	$J=2\to3$,	$K=2\to2$,	$F=3\to4$ $F=3\to3$ $F=3\to2$	47,088.69
	$J=2\to3$,	$K=2\to2$,	$F=2\to3$ $F=2\to2$	47,087.39

[a] Frequency is for ground vibration state unless otherwise specified.

tures are:

$$I_B = \tfrac{3}{2}M_H(d_{CH}\sin\alpha)^2 + 1/M\{d_{C'N}{}^2 M_N(M-M_N)$$
$$+ d_{CC'}{}^2(M_N+M_{C'})(M_C+3M_H)$$
$$+ 3(d_{CH}\cos\alpha)^2 M_H(M-3M_H)$$
$$+ 2d_{C'N}d_{CC'}M_N(M_C+3M_H)$$
$$+ 6d_{C'N}d_{CH}\cos\alpha M_N M_H$$
$$+ 6d_{CC'}d_{CH}\cos\alpha M_H(M_N+M_{C'})\}$$

for CH₃CN, and

$$I_B = \tfrac{3}{2}M_H(d_{CH}\sin\alpha)^2 + 1/M\{d_{NC'}{}^2 M_{C'}(M-M_{C'})$$
$$+ d_{CN}{}^2(M_{C'}+M_N)(M_C+3M_H)$$
$$+ 3(d_{CH}\cos\alpha)^2 M_H(M-3M_H)$$
$$+ 2d_{NC'}d_{CN}M_{C'}(M_C+3M_H)$$
$$+ 6d_{NC'}d_{CH}\cos\alpha M_{C'}M_H$$
$$+ 6d_{CN}d_{CH}\cos\alpha M_H(M_{C'}+M_N)\}$$

for CH₃NC, where I_B is the moment of inertia about an axis perpendicular to the figure axis, M is the mass of the molecule, α is the angle between the C—H bond and the figure axis. (C' designates the carbon atom adjacent to the nitrogen in CH₃CN and the terminal carbon atom in CH₃NC.) All the remaining symbols have the usual significance. For the isotopic species the appropriate masses were substituted in the above expressions, and the distances and angles found from the resulting simultaneous equations.

IV. DISCUSSION OF THE STRUCTURES

It is of interest that the CH lengths and bond angles to the C are, within the limits of error, equivalent to those in methane. This is true also for the CH₃ group of methyl alcohol,[11] and approximately true for the methyl halides.[12] Such uniformity in the configuration of the CH₃ group in organic compounds has been generally assumed, but before the development of microwave spectroscopy this assumption could not be widely tested. Electron diffraction, the principal method then used for determining the structures of organic molecules, did not, in general, locate the hydrogen atom.

The CC bond found for H₃C—C≡N is 0.03A shorter than the previously reported electron diffraction value, and is 0.08A shorter than the CC bond in ethane and similar hydrocarbons. The effective single-bond radius of C joined by a triple bond is smaller by about 0.03A than the usual single-bond C radius. The additional shortening can be accounted for by a contribution of about 10 percent to the ground state of the molecule

[11] Edwards, Gilliam, and Gordy (unpublished results).
[12] Gordy, Simmons, and Smith, Phys. Rev. 74, 243 (1948).

TABLE II. Comparison of calculated and observed hyperfine structure for the $J=1\rightarrow2$ transition of $C^{12}H_3C^{12}N^{14}$.

K	$F\rightarrow F'$	Frequency in Mc/sec. Calc.[a]	Obs.	Relative intensity Calc.	Obs.
0	$1\rightarrow1$	36,797.51	36,797.52	18	20
0	$2\rightarrow1$	36,796.20	36,796.27	1	15
1	$0\rightarrow1$	36,796.25		18	
0	$2\rightarrow3$	36,795.42		100	
0	$1\rightarrow2$	36,795.33	36,795.38	54	160
1	$2\rightarrow1$	36,795.27		1	
1	$2\rightarrow3$	36,794.88	36,794.88	75	70
1	$1\rightarrow1$	36,794.62	—	13	—
0	$0\rightarrow1$	36,794.24	36,794.26	24	25
1	$2\rightarrow2$	36,794.19		13	
0	$2\rightarrow2$	36,794.02	—	18	—
1	$1\rightarrow2$	36,793.55	36,793.64	40	30

[a] Calculated with $eQ(\partial^2V/\partial z^2) = -4.35$ Mc/sec. and $D_{JK} = 0.18$ Mc/sec.
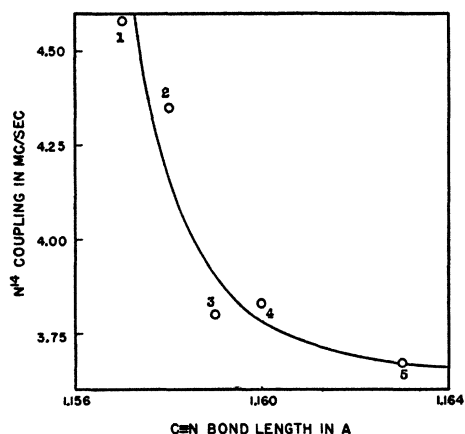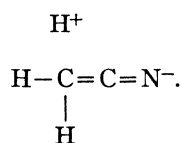

FIG. 1. Relation of the $C\equiv N$ bond length to the N^{14} nuclear quadrupole coupling in $XC\equiv N$ compounds. (1) Represents HCN, (2) CH$_3$CN, (3) ICN, (4) BrCN, (5) ClCN.

by hyperconjugated structures of the type:

$$H^+$$
$$H-C=C=N^-.$$
$$|$$
$$H$$

This amount of hyperconjugation would have a negligible effect on the CN and CH lengths, but should decrease the nuclear coupling of the N^{14} a measurable amount. The magnitude of coupling found for N^{14} is 0.23 Mc/sec. less than that in hydrogen cyanide. Figure 1 shows the variation of the N^{14} coupling with the CN length for all the cyanides so far studied with microwave spectroscopy.

TABLE III. Molecular constants.

Molecule	B_0 Mc/sec.	I_B $\times10^{-40}$ g cm^2	D_{JK} Mc/sec.	$eQ(\partial^2V)/(\partial z^2)$ for N^{14} Mc/sec.
$C^{12}H_3C^{12}N^{14}$	9198.83	91.20$_{34}$	0.17$_8$	-4.35 ± 0.20[a]
$C^{12}H_3C^{13}N^{14}$	9194.28	91.24$_{86}$	—	-4.35
$C^{12}D_3C^{12}N^{14}$	7857.93	106.76$_{66}$	0.11$_3$	-4.35
$C^{12}D_3C^{13}N^{14}$	7848.51	106.89$_{48}$	0.11$_0$	-4.35
$C^{12}H_3N^{14}C^{12}$	10,052.90	83.45$_{50}$	0.22$_3$	$<|0.5|$
$C^{12}H_3N^{14}C^{13}$	9695.91	85.52$_{77}$	—	$<|0.5|$
$C^{12}D_3N^{14}C^{12}$	8582.06	97.75$_{79}$	0.14$_1$	$<|0.5|$
$C^{12}D_3N^{14}C^{13}$	8278.79	101.33$_{91}$	0.13$_0$	$<|0.5|$

[a] This value is smaller than the preliminary one given in reference 5.

TABLE IV. Molecular structures.

	d_{CH}	d_{CC}	d_{CN}	$\angle$HCH
CH$_3$CN	1.092A	1.460A	1.158A	109°8'

	d_{CH}	d_{CN}	d_{NC}	$\angle$HCH
CH$_3$NC	1.094A	1.427A	1.167A	109°46'

The early electron diffraction value for the CN length in CH$_3$NC, 1.48A, found by Brockway[3] was revised downward by the remeasurements of Gordy and Pauling.[4] The present microwave work revises this distance further downward to 1.427A. This is some 0.05A shorter than the usual CN single bond. If we assume, as for C, a shortening of the nitrogen single bond radius of 0.03A by the adjacent multiple bond, there is still a shortening of 0.02A to be accounted for. Hyperconjugated structures of type III are probably not very important because of the unstable charge distribution.[4]

$$\begin{array}{ccc} H & H & H^+ \\ | & | & \\ H-C-N^+\equiv C^- & H-C-N=C & H-C=N^+=C^= \\ | & | & | \\ H & H & H \\ I & II & III \end{array}$$
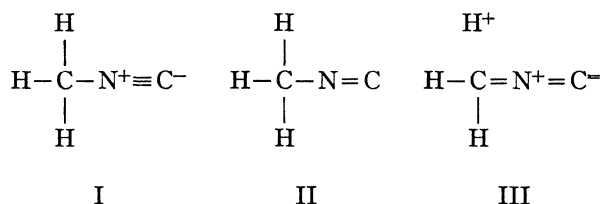
It seems more likely that the shortening of the CN bond is due to a decrease in the nitrogen radius because of the positive formal charge on N in the most important structure type I. The NC length is slightly longer than the CN length in HCN or CH$_3$CN. This might be explained by postulating contribution from structure II. However, very significant contributions from II are precluded by the linear configuration of CNC and by the absence of detectable N^{14} hyperfine structure for this molecule. In structures I and III the valence orbitals of N are symmetrically filled and, if distortion effects are neglected, $(\partial^2V)/(\partial z^2)$ would be zero.